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1.	Your reference	MRR 1565 GB
2.	Patent application number *(The Patent Office will fill in this part)*	0219681.4
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	(1) ANGLO PLATINUM LIMITED of 28 Harrison Street, Marshaltown, 2107, South Africa and 83764360001 (2) THE UNIVERSITY OF STRATHCLYDE of 16 Richmond Street, Glasgow G1 1XQ, Scotland
	Patents ADP number *(if you know it)*	408166700l
	If the applicant is a corporate body, give the country/state of its incorporation	(1) South Africa (2) Scotland
4.	Title of the invention	CHROMATOGRAPHIC MEDIUM
5.	Name of your agent *(if you have one)*	IAN CARMICHAEL WISHART
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	JOHNSON MATTHEY TECHNOLOGY CENTRE BLOUNTS COURT SONNING COMMON READING RG4 9NH
	Patents ADP number *(if you know it)*	825673100l

		Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
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		Number of earlier application	Date of filing *(day / month / year)*
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Abstract	1
Drawing(s)	4 +4

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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	ONE
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date 22.8.02

I C WISHART

12. Name and daytime telephone number of person to contact in the United Kingdom

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DUPLICATE

CHROMATOGRAPHIC MEDIUM

This invention concerns chromatographic media, more especially it concerns chromatographic media comprising polymer-supported thioether ligands, methods for their preparation, and their use in the separation of metals, particularly the platinum group metals.

Chromatography has been suggested for the interseparation of platinum group metals ("PGM" – platinum, palladium, rhodium, osmium, ruthenium and iridium). The earliest suggestion was in USP 4855143. However, it was found that the media recommended therein exhibited serious degradation in the concentrated acid necessarily used for solutions of the PGM. Later, USP 5879644 taught the use of selected commercial media, especially "Toyopearl", for the interseparation of the PGM. These, especially when combined with certain process improvements, provided good separation and beneficial lifetimes however, capacity was found to be low and high volumes of eluant are required leading to increased costs. The chromatographic separation process appears to offer great promise for PGM refining. There remains, however, the need for further improved media, especially for the recovery or separation of palladium. Very many commercial media have been tested but none has exhibited the desired combination of properties namely, increased throughput and good metal separation per unit volume of eluant.

The use of solid phase extraction is commonplace in PGM separation and refining. For example, the use of specified thioethers has been recommended for the extraction of Pd from nitric acid solutions of plutonium arising from the nuclear industry (USP 5,171,546). USP 4,959,153 proposes the binding of thioether-based materials linked to silica, and we believe that these have been introduced into commercial PGM refining processes and are marketed as "Superlig". Such solid phase extractant materials demonstrate fast binding of Pd but, the use of an inorganic support (silica) means that their capacity is rather low, and tests have shown almost halving of capacity after three month's use.

In accordance with the present invention, a chromatographic medium comprises thioether ligands bound to a solid cross-linked polymer matrix; wherein the polymer is organic; and wherein the medium is hydrophilic.

In the present invention, a distinction is drawn between media which have chromatographic function and those which simply absorb species from solution. A chromatographic medium is one which is able to separate one or more species from a mixed solution in a sequential fashion. By way of contrast, a solid phase extraction medium can be used to effectively extract species from solution but has no capacity for separation. For example, the commercial 'Superlig' materials selectively extract and bind one or more species from a mixed solution but they do not separate the species remaining in solution. Complete separation can only be effected by successively passing the mixed solution through a series of different materials, each one tailored to extract and bind a particular species or group of species. Recovery of each species is by elution. Furthermore, the use of an organic polymer support provides the media of the present invention with higher capacity compared to those which use inorganic supports.

Preferably, the polymer comprises methacrylate moieties, styrene moieties, poly(ethylene glycol) moieties or any combination or mixture thereof.

The ligands may be bound to the polymer matrix through a branched or an unbranched group. Suitable groups include alkyl, aryl, aralkyl, ether or ester groups or combination thereof. Such groups may be unsubstituted but are preferably substituted. It is particularly preferred that groups are substituted by hydroxyl groups to improve the hydrophilicity of the medium.

Additionally, the sulphur atom of the thioether group may be substituted by an alkyl group. Suitable alkyl groups may have from 1 to 6, preferably 2 to 4, carbon atoms and are optionally substituted. Hydroxyl groups are particularly preferred as substituents although other groups which promote hydrophilic properties are also suitable.

The ligands used in the present invention may comprise mono-, di- or poly-thioether ligands, with mono-thioether ligands being particularly preferred.

The medium may further comprise additional substituent groups bound to the polymer matrix. These may provide the medium with improved hydrophilicity. Examples of suitable ligands include water soluble groups, or groups which can interact with water via hydrogen bonding, such as poly-ethylene glycols, poly-propylene glycols, hydrophilic polyacids and poly-ether, -ester or –hydroxy species.

The medium may be in any solid form however, preferably the medium is in the form of a gel or a porous solid. Beads, films and fibres are preferred.

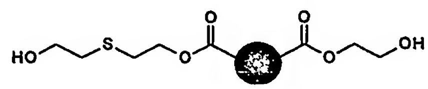
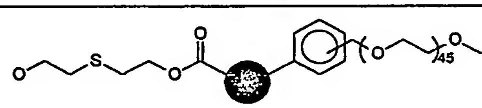
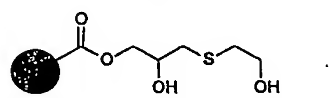
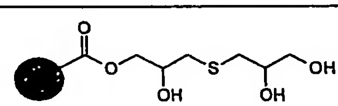
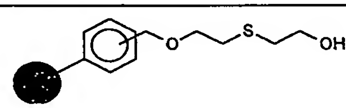
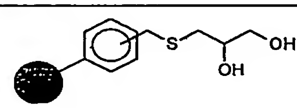
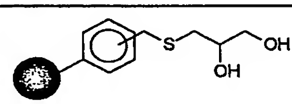
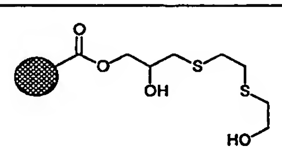
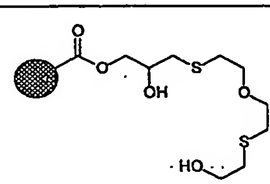
A particular advantage of the media of the present invention is that they do not degrade significantly in strong acid solutions. This makes them suitable for use in the recovery of PGMs from hydrochloric acid solutions.

The polymer matrix may be pre-formed or may be synthesised during the formation of the medium, and the matrices may be cross-linked to a lesser or greater extent. Low levels of cross-linking, of the order of 1-10%, produce a gel-type product, whereas higher levels of cross-linking, e.g. of the order of 50-70% or even higher, used in combination with a suitable porogen (pore former) produce a rigid material. Porogens are known in the art and include species such as water and xylene. Such rigid materials do not exhibit gel-type swelling in aqueous media but, will readily sorb aqueous solutions into the permanent pore structure without significant volume swelling. The polymers preferably incorporate methacrylate and/or styrene moieties. When glycidyl methacrylate resins are used as precursor resins, at least one hydroxyl group is desirably present on the reactive thiol such that at least two hydroxyl groups are present after the reaction between the thiol and glycidyl group.

It is considered that the presence of poly(ethylene glycol) groups is particularly beneficial to the rate of uptake of Pd from HCl solutions.

Structural representations of some examples of media according to the present invention are shown in Table 1.

Table 1

Code	Structural representation	Polymer matrix
FB131		methacrylate
FB138		methacrylate-co-styrene
FB143		methacrylate
FB190		methacrylate
FB194b		styrene
FB205		styrene
FB206		styrene
FB173		methacrylate
FB202		methacrylate

 = porous-type resin  = gel-type resin

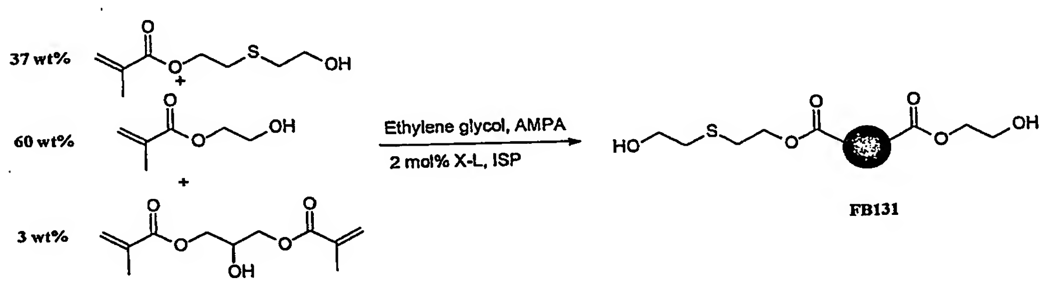
The present invention also provides a method of manufacturing a chromatographic medium comprising reacting a functionalised thioether monomer with a hydrophilic monomer in the presence of a cross-linking agent. Suitable cross linking agents are known in the art and include species such as 3-(acryloyloxy)-2-hydroxypropyl methacrylate, glycerol dimethacrylate, ethylene glycol dimethacrylate and poly(ethylene glycol) dimethacrylate.

In an alternative embodiment, a method of manufacturing a chromatographic medium comprises reacting a thiol with a functionalised polymer.

The method of the invention is illustrated by the following reaction schemes:

Scheme 1

Copolymerisation of a thioether functionalised monomer with hydrophilic monomers.



AMPA = 2,2'-azobis(2-methylpropionamide)dihydrochloride)

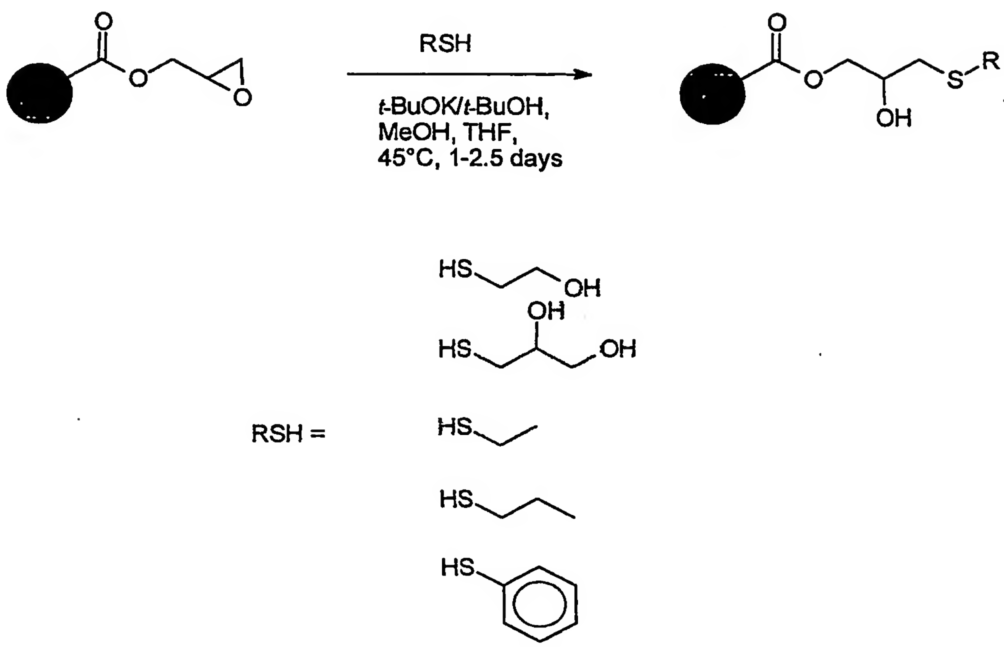
Scheme 2

Reaction of thiols with reactive polymers

Reaction with Macroprep Epoxide™ [poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate)]

Surface area of Macroprep Epoxide™ = 18 $m^2.g$ (N_2 BET)

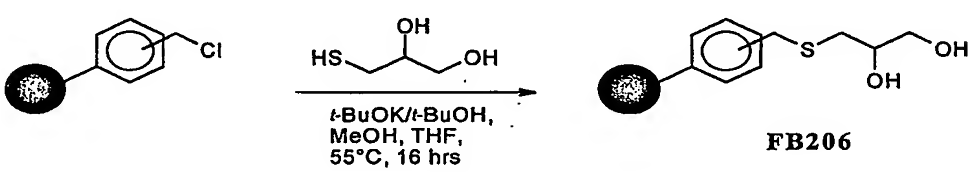
Loading capacity of Macroprep Epoxide™ = 4 mmol epoxide/g



Scheme 3a

Reaction with poly(vinylbenzyl chloride-co-divinylbenzene) resins:

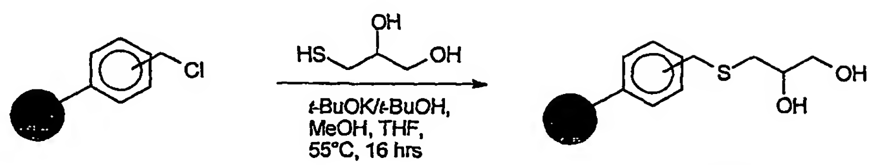
Gel type resin (2% X-linked) 5.9 mmol/g Cl



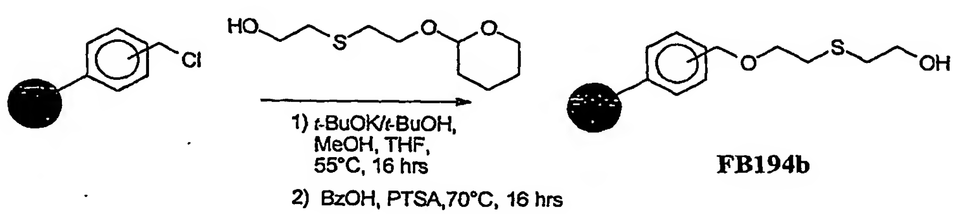
FB206

Scheme 3b

High surface area resin (62.5% X-linked) 2.1 mmol Cl/g
Surface area = 350 m^2/g (N_2 BET)



FB205



FB194b

The method of the invention may be carried out by the skilled polymer chemist using conventional techniques and conditions.

The invention further provides a process for the separation of components from solution, comprising passing said solution over a chromatographic medium according to the invention. Preferably, the solution is a solution comprising a PGM or several of them, e.g. in admixture with a proportion of base metals, especially a solution containing Pd. Such solutions may be PGM refinery streams, side-streams or other solutions containing Pd including so-called secondary refining streams arising from the recycling or recovery of used catalysts or other materials.

In a particularly preferred embodiment, the solution to be separated comprises Pd together with other PGM and/or base metals. Conventionally, it is difficult to use chromatography to obtain substantially pure Pd from a mixed PGM solution at high metal loading. This is because as metal loading increases the elution peaks for Pd and Pt overlap. A further process step is thus required, leading to increased costs and plant space. The present invention overcomes this problem by simultaneously retaining Pd whilst chromatographically separating other metals. Only a single process step is required even at high metal loadings

Although the media of the invention are considered to offer particular advantages in the treatment of Pd-containing solutions, they are not to be considered as limited thereto.

The invention will now be described by way of example only and with reference to the following drawings in which:

Figure 1 is a graph illustrating the rate of uptake of Pd in a 6M hydrochloric acid solution by some examples of media according to the present invention;

Figure 2 is a graph illustrating the rate of uptake of Pd in a 6M hydrochloric acid solution by a media with limited hydrophilicity and also some examples of hydrophobic media not according to the present invention;

Figure 3 is a graph comparing the rate of uptake of Pd from 0.6M and 6M hydrochloric acid solution by one example of a medium according to the present invention;

Figure 4 is a graph comparing the rate of uptake of Pd from 0.6M and 6M hydrochloric acid solution by a further example of a medium according to the present invention;

Figure 5 is a chromatogram showing the separation of PGM in a mixed PGM solution using one of the media of Fig. 1;

Figure 6 is a chromatogram showing the separation of PGM in a mixed PGM solution using the medium of Fig. 4;

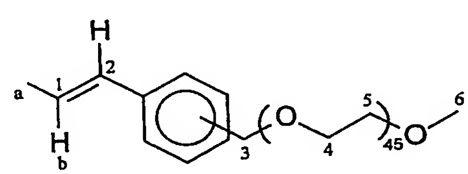
Figure 7 is a chromatogram showing the separation of PGM in a mixed PGM solution which also include Ag and Cu using the medium of Fig. 4, and;

Figure 8 shows the elution of substantially pure Pd using ammonia from the medium of Fig. 4.

Some preparative routes to yield the media of the invention are described below. The routes described are illustrative and as such, are not intended to limit the scope of the present invention. Alternative synthetic strategies will be known to those skilled in the art

EXAMPLE 1

Preparation of vinylbenzyl poly(ethylene glycol) 2000 methyl ether

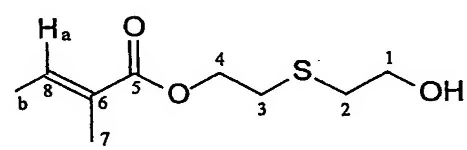


A 1.0 M solution of potassium *tert*-butoxide in 2-methyl-2-propanol (375 ml; 0.375 mol) was added to a solution of poly(ethylene glycol) monomethyl ether *av.* M_w = 2000 (598 g; 0.299 mol) in THF (1000 ml). The solution was stirred for 30 minutes at ambient temperature. Vinylbenzyl chloride (65 g; 0.426 mol) was added to the solution which was stirred at 45 °C for 16 hrs. The solution was neutralised with acetic acid (1 ml) and hydroquinone (0.1 g) was added prior to reducing the volume to 700 ml by vacuum distillation at 55 °C. The concentrated solution was then added to diethyl ether (1000 ml) and kept at 4 °C for 16 hrs. The precipitates thus formed were filtered and

washed with diethyl ether and n-hexane and dried on a rotary evaporator at 50 °C. The organic-soluble products were extracted in acetone at 50 °C and separated by filtration through a sintered glass frit (P3) with the aid of Celite™. Vinylbenzyl poly(ethylene glycol) 2000 methyl ether (548 g; 259 mol; 87% yield) was recovered from the acetone solution after drying at 57 °C under vacuum for 2 hrs. The molten VBPEG 2000me was poured into a 40x20 cm stainless steel tray and allowed to solidify before processing into small (4x10x10 mm) blocks.

EXAMPLE 2

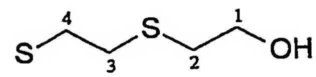
Preparation of thiodiethanol monomethacrylate (TDEMA)



A solution of methacryloyl chloride (16.7 g; 0.160 mol) in dichloromethane (100 ml) was added dropwise at 5 °C to a solution of thiodiethanol (20 g; 0.164 mol) and triethylamine (33.7 g; 0.334 mol) in dichloromethane (50 ml). After addition was complete, the solution was stirred at ambient temperature for 16 hrs. The excess triethylamine was neutralised with glacial acetic acid and the volume reduced on a rotary evaporator. The soluble organic products were extracted in diethyl ether and separated by filtration. Thiodiethanol monomethacrylate was purified by preparative flash chromatography, using silica gel (eluent = 1:1 diethyl ether : hexane). Fractions containing pure product were collected and combined to yield thiodiethanol monomethacrylate (8.5 g; 0.044 mol, 28% yield) as a light coloured oil. Several attempts at distillation of TEDMA at reduced pressure and in the presence of excess stabiliser resulted in rapid polymerisation of the monomer. Thiodiethanol monomethacrylate was stored at 4 °C in the presence of 100 ppm 3,5-di-*tert*-butylcatechol.

EXAMPLE 3

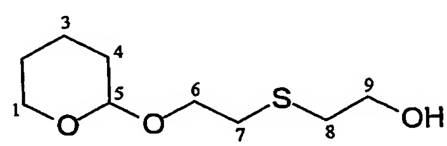
Preparation of 2-(2-mercapto-ethylsulfanyl) ethanol



1,2-Ethane dithiol (20.79 ml; 0.248 mol) was added to a solution of sodium hydroxide (9.92 g; 0.248 mol) in ethanol (200 ml) and stirred for 15 min. 2-Chloroethanol (16.65 ml; 0.248 mol) was added to the solution at ambient temperature and after addition was complete the solution was heated to 80 °C and stirred for 2 hrs. The reaction mixture was then cooled to ambient temperature and a small amount of acetic acid (1 ml) added to neutralise the solution. The insoluble sodium chloride was separated by filtration and the filtrate transferred to a distillation apparatus. Ethanol and unreacted 1,2-ethane dithiol were removed under reduced pressure prior to the fractional distillation of 2-(2-mercapto-ethylsulfanyl) ethanol at 98 °C and 0.4 mbar. Pure fractions were combined to afford 2-(2-mercapto-ethylsulfanyl) ethanol (13.8 g; 0.1 mol; 40% yield) as a colourless liquid possessing a mild stench.

EXAMPLE 4

Preparation of monotetrahydropyranyl thiodiethanol

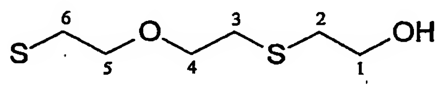


A solution of 3,4-dihydro-2 *H*-pyran (10g; 0.118 mol) in dichloromethane (10 ml) was added dropwise to a solution of thiodiethanol (14.5 g; 0.118 mol) and PTSA (0.01 g) in dichloromethane (10 ml) at room temperature. After stirring for 2 hrs triethylamine (0.1 ml) was added to neutralise the acid catalyst. The organic phase was washed with aqueous 0.1% NaOH (50 ml). Distillation of the organic phase at 99 °C and 0.07 mbar resulted in a mixture of the di- and mono-protected acetals. Purification by

flash chromatography using diethylether : hexane (1:1) afforded monotetrahydropyranyl thiodiethanol (7.2 g; 0.035 mol; 30% yield) as a light yellow oil.

EXAMPLE 5

Preparation of 2-[2-(2-mercapto-ethoxy)-ethylsulfanyl]-ethanol



2-Mercaptoethyl ether (53.8 ml; 0.434 mol) was added to a solution of sodium hydroxide (17.36 g; 0.434 mol) in ethanol (300 ml) at ambient temperature and stirred for 15 min. 2-Chloroethanol (29.1 ml; 0.434 mol) was added to the solution at ambient temperature and after addition was complete the stirred solution was heated to 80 °C for 1 hr. The reaction mixture was then cooled to ambient temperature and the solid sodium chloride separated by filtration. The filtrate was transferred to a distillation apparatus and ethanol and unreacted 2-mercaptoethyl ether removed under vacuum (the latter distilling at 62 °C and 0.4 mbar). Fractional distillation of the remaining product yielded 2-[2-(2-mercapto-ethoxy)-ethylsulfanyl]-ethanol at 128 °C and 0.3 mbar. Pure fractions were combined to afford 2-[2-(2-mercapto-ethoxy)-ethylsulfanyl]-ethanol (31 g; 0.17 mol; 39% yield) as a colourless oil.

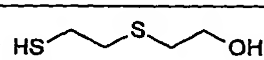
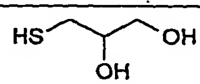
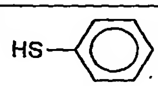
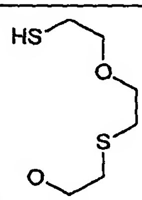
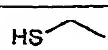
EXAMPLE 6

Reaction of thiols with Macroprep Epoxide®

The reaction of thiols with Macroprep Epoxide® was carried out under basic conditions using a 1.0 M solution of potassium *tert*-butoxide in 2-methyl-2-propanol as base. The ratio of base : thiol : resin was varied for the series of thiols used and the ratios are presented along with other reaction conditions in Table 2. The 1.0 M solution of potassium *tert*-butoxide was added to a solution of the thiol in methanol : THF (1:1). This solution was added to a slurry of the previously dried resin in methanol : THF (1:1) at ambient temperature. The slurry was stirred by means of an overhead stirrer from 16 to 48 hr at various temperatures. The reaction mixture was then cooled to ambient

temperature, filtered and washed successively with methanol aqueous acetic acid, water, acetone and finally diethyl ether. The resin was dried at 70-80 °C under vacuum for at least 2 hrs.

Table 2: Stoichiometries and reaction conditions for the reaction of thiols with Macroprep Epoxide®

Resin Code	Thiol	Mol Ratio base : thiol : resin	Reaction Temp. (°C)	Reaction Time (hrs)	Resin : Solvent ratio (g:ml)
FB143		1 : 1.4 : 0.64	45	48	1 : 7.5
FB173		1 : 2.5 : 2	50	24	1 : 8
FB190		1 : 4.2 : 3.2	45	16	1 : 6.3
FB191		1 : 4.2 : 3.2	45	16	1 : 6.3
FB192		1 : 3.3 : 2.5	45	16	1 : 7
FB202		1 : 7.5 : 6.3	45	24	1 : 7.8
FB204		1 : 27 : 4.8	ambient	18	1 : 6.7

EXAMPLE 7

Preparation of FB131 and FB138 by inverse suspension polymerisation

The continuous phases for the inverse suspension polymerisations (ISP) were prepared by dissolving the ethyl ester of a maleic anhydride-*co*-octadecene copolymer Mw 50 000 (Et-MAO) in liquid paraffin (LP) or mixtures of liquid paraffin and cyclohexane. In cases where only the former solvent was used heating at 140-160 °C with continuous stirring for 1 hr was required to obtain complete dissolution of the stabiliser. All solutions were cooled to room temperature before addition to the

suspension polymerisation reactor. The continuous phases were degassed inside the sealed reactor by bubbling nitrogen through the solutions at 65 °C for 1 hr. The monomer phases were kept under nitrogen for 5 min. prior to addition to the continuous phases at 42 °C. Suspensions were formed by stirring the two phases at around 300 rpm for a period of 10-15 min. and thereafter the temperature was increased to 65 °C, with continuous stirring for 6 hrs. The resins were then filtered, washed with hexane, and extracted in a Soxhlet apparatus with acetone for 16hrs. Finally the resins were washed with diethyl ether before being vacuum dried. The monomer phase compositional data and inverse suspension polymerisation conditions for FB131 and FB138 are presented in Tables 3 and 4.

Table 3: Monomer phase composition data for FB131 and FB 138

Resin Code	Mass (g) TDEMA	Mass (g) HEMA	Mass (g) VBPEG 2000 me	Mass (g) GDMA	Mass (g) AMPA	Mass (g) H_2O	Mass (g) Ethylene glycol
FB131	4.38	7.0	-	0.36	0.13	0.50	5.0
FB138	2.8	-	4.88	0.5	0.09	0.35	3.5

(HEMA = hydroxy ethyl methacrylate; VBPEG = vinyl benzyl polyethylene glycol; GDMA = glycol dimethacrylate)

Table 4: Conditions used in the ISP of FB131 and FB 138

Resin Code	Continuous phase	Stirrer speed (rpm)	Yield isolated (%)
FB131	Et-MAO (0.4 g) / LP (150g) / cyclohexane (70 g)	268	95
FB138	Et-MAO (0.17 g) / LP (170 g)	300	nr

EXAMPLE 8

Preparation of poly(vinylbenzyl chloride (VBC)-*co*-styrene-*co*-divinylbenzene(DVB)) resin beads via suspension polymerisation

A 0.5% aqueous solution of 88% hydrolysed polyvinyl alcohol (700 ml) was introduced into a 1000 ml baffled reaction vessel and allowed to stand under a nitrogen atmosphere for 30 min. Monomer phase (50 ml) containing 1 wt% AIBN was degassed by bubbling nitrogen through the solution for 10 min. The monomer phase was added to the aqueous phase at 20 °C and agitated by means of a propeller type stirrer at an appropriate velocity so as to obtain monomer droplets of approximately 100 μm diameter. After stirring for 20 min at 20 °C, the temperature was increased to 80 °C and stirred for a further 6 hrs. The mixture was filtered hot, and washed with water until the washings were clear. The filter was washed with methanol and the resin beads extracted in a Soxhlet apparatus with acetone for 16 hrs. Macroporous resins were dried in a vacuum oven at 40 °C for 16 hrs. Gel-type resins were washed with methanol prior to drying, so as to prevent adhesion of beads during drying. The conditions for the suspension polymerisation of the vinylbenzyl chloride based resins are presented in Table 5.

Table 5: Conditions for the suspension polymerisation of VBC -*co*-St-*co*-DVB

Resin Code	Monomer composition (vol.%)	Porogen (volumetric porogen: monomer)	Stirrer speed (rpm)	Yield (%)
R1	98% VBC 2% DVB	–	500	53
R2	37.5% VBC 62.5% DVB	Xylene (1 : 1)	600	81
R3	37.5% VBC 25.0% DVB 37.5% Styrene	2-ethyl-hexanol (1 : 1.35)	600	73

EXAMPLE 9

Reaction of 3-mercapto-1,2-propanediol with R2 (= FB205)

A 1.0 M solution of potassium *tert*-butoxide in 2-methyl-2-propanol (20 ml; 20 mmol) was added to a solution of 2-mercapto-1, 2-propanediol (3.24 g; 30 mmol) in 1 : 1 methanol : THF (20 ml). The solution was stirred at ambient temperature for 5 min. before addition to a slurry of resin R2 (4 g; 10.67 mmol) in 1:1 methanol : THF (40 ml). The slurry was stirred at 50 °C for 16 hr. After cooling the reaction mixture the resin was filtered and washed with a 10 : 1 : 10 solution of methanol : acetic acid : water (300 ml). The resin was then washed successively with methanol (100 ml), acetone (100 ml) and diethyl ether (100 ml). The resin was dried at 70 °C under high vacuum for 2 hrs.

EXAMPLE 10

Reaction of 3-mercapto-1,2-propanediol with R1 = (FB206)

A 1.0 M solution of potassium *tert*-butoxide in 2-methyl-2-propanol (20 ml; 20 mmol) was added to a solution of 2-mercapto-1, 2-propanediol (2.9 g; 27.7 mmol) in 1:2 methanol : THF (60 ml). The solution was stirred at ambient temperature for 5 min. before addition of resin R1 (3 g; 18.3 mmol). The slurry was heated to 55 °C for 16 hrs. After cooling the reaction mixture the resin was filtered and washed with a 10:1:10 solution of methanol : acetic acid : water (300 ml). The resin was then washed successively with 19:1 methanol : water (100 ml) and water (100 ml). The resin was dried at 70 °C at 0.1 mbar for 5 hrs.

EXAMPLE 11

Reaction of monotetrahydropyranyl thiodiethanol with R2 (= FB194)

A 1.0 M solution of potassium *tert*-butoxide in 2-methyl-2-propanol (16 ml; 16 mmol) was added to a solution of monotetrahydropyranyl thiodiethanol (4.4 g; 21.6 mmol) in THF (15 ml). The solution was stirred at ambient temperature for 15 min. before being added to a slurry of resin R2 (4 g; 10.8 mmol) in THF (5 ml). The reaction mixture was heated at 72 °C for 16 hr without stirring. The resin was filtered and washed

successively with methanol, water, acetone and then methanol. The resin was dried at 70 °C under high vacuum for 2 hrs.

EXAMPLE 12

Cleavage of the tetrahydropyranyl group from Example 11 (= FB194b)

The product of Example 11 (3.5 g) was added to a solution of PTSA (0.1 g) in benzyl alcohol (15 ml. The slurry was heated at 70 °C for 16 hr. Upon cooling, the slurry was filtered and the resin washed successively with chloroform, acetone and methanol. The resin was dried at 70 °C under high vacuum for 2 hr.

The media according to the invention effectively bind Pd from strong (about 6M) HCl solutions of mixed PGMs. The results obtained in preliminary binding tests from a simple solution of Pd, are shown in Fig. 1. Media FB 138, 143, 190 and 131 showed fast and complete Pd uptake. Fig 2 shows some examples of media which are essentially hydrophobic (1, 2, 3); these show slow and incomplete Pd uptake. The better result in Fig 2, relating to FB194b (4), is attributed to the medium having a single hydroxyl group substituent which provides some limited hydrophilicity.

Further tests have been carried out on media FB 143 and FB 138, at a lower HCl concentration of 0.6M as well as at 6M HCl. The results of these tests are plotted in Figs 3 and 4 respectively.

Tests have been carried out to assess both the total loading capacity of the media for Pd, and the rate of binding, the results of which are set out in Table 6 below. The $t_{1/2}$ value refers to the time taken for the media to reach half of its theoretical capacity based on the sulphur content.

Table 6: Pd loading capacities and $t_{1/2}$ for resins supporting monothioether ligands.

Medium	mmol S/g	$t_{1/2}$	Pd loading capacity (mmol Pd/g resin)	Molar ratio Pd : S
FB131	1.9	8 min.	1.18	1:1.6
FB138	1.9	<3 min.	1.27	1:1.5
FB143	3.0	<3 min.	1.76	1:1.7
FB190	2.9	<3 min.	1.73	1:1.7
FB194b	0.75	2 hrs	0.35	1:2.1
FB205	1.6	<3 min.	0.73	1:2.2
FB206	4.2	45 min.	2.19	1:1.9

The skilled person will realise that the speed of loading is important for practical use of Pd binding media, as is the total loading capacity, because this affects both the total quantity of medium required and throughput, and consequently the size of a plant and the capital cost thereof. For example, medium FB 206 is believed to have a total loading capacity which is a factor of approximately 5 greater than the commercial "Superlig" material. This may offer also the possibility of less washing required, which in turn lessens the amount of effluent produced thereby minimising environmental pollution.

The preferred media of the invention were tested by loading 0.25 ml of a commercial mixed PGM process stream having the composition shown in Table 7, over a test chromatography column of 200 mm length and 5 mm id, and eluting with 6M HCl at a rate of in the case of FB131 0.375 ml/min and in the case of FB138 a rate of 0.385 ml/min, and the eluted stream is analysed for the PGM by ICP-ES The area of the peaks is not an accurate measure of the concentration of each metal ion but, is an approximation of the relative concentrations. The results are plotted in Figs 5 and 6. In both cases, no Pd could be detected in the eluted liquor. In Fig 6, there is a Pt peak that overlaps only to a very small extent with Os, and is quite distinct from the mixed peak of Rh, Ru and Ir, the so-called "insoluble metals".

The data presented in Fig.7 reproduce those of Fig. 6 but using a solution including base metal contamination in the form of Ag and Cu. There is some contamination of the Pt peak with Ag. It is postulated that the amount of sulphur on the medium affects the degree of retention of these metals.

Thus, the resin media of the invention are effective to remove Pd from mixed PGM solutions. The Pd may be recovered by elution with ammonia solution, or a solution of a nitrogen-containing species such as thiourea, ammonium thiocyanate or an amine, and Fig 8 demonstrates the clean peak of recovered Pd that can be obtained from the resin media of the invention when extracting using aqueous ammonia.

The skilled person will realise that many variations of the present invention herein particularly described can be accomplished without departing from the essential inventive scope thereof.

Table 7: Composition of PGM concentrate

Element	Concentration (g/l)
Ag	0.643
Al	<0.001
As	0.796
Au	0.248
Ca	0.036
Co	0.608
Cr	0.130
Cu	24.728
Fe	0.004
Ir	4.029
Mg	0.017
Mn	0.007
Mo	<0.001
Na	1.457
Ni	32.217
Os	5.271
Pb	2.932
Pd	56.924
Pt	96.023
Rh	14.378
Ru	18.278
S	23.349
Sb	<0.001
Sc	0.090
Se	0.376
Sn	<0.001
Te	<0.001
Zn	<0.001

CLAIMS

1. A chromatographic medium, the medium comprising thioether ligands bound to a solid cross-linked polymer matrix; wherein the polymer is organic; and wherein the medium is hydrophilic.

2. A medium according to claim 1, wherein the thioether ligands comprises monothioether ligands.

3. A medium according to claim 1 or claim 2, wherein the polymer comprises methacrylate moieties, styrene moieties, poly(ethylene glycol) moieties or any combination or mixture thereof.

4. A medium according to any preceding claim, wherein the ligands are bound to the polymer matrix through a branched or unbranched alkyl, aryl, aralkyl, ether or ester group or combination thereof, optionally substituted, especially by hydroxyl.

5. A medium according to any preceding claim, wherein the sulphur atom of the thioether group is substituted by an alkyl group of 2 to 4 carbon atoms, optionally substituted, especially by hydroxyl.

6. A medium according to any preceding claim, in the form of a gel or a porous solid.

7. A chromatographic medium substantially as hereinbefore described.

8. A method of manufacturing a medium according to any one of the preceding claims, the method comprising reacting a functionalised thioether monomer with a hydrophilic monomer in the presence of a cross-linking agent.

9. A method of manufacturing a medium according to any of claim 1 to 7, the method comprising reacting a thiol with a functionalised polymer.

10. A process for the separation of components from solution, the process comprising passing said solution over a medium according to any of claims 1 to 7.

11. A process according to claim 10, wherein the solution comprises one or more PGM.

12. A process according to claim 11, wherein the solution comprises Pd; and wherein said Pd is retained on the medium.

13. A process according to any of claims 10 to 12, wherein the solution comprises Pd in admixture with two or more other metals; and wherein the medium retains the Pd whilst chromatographically separating the two or more other metals.

14. A process according to claim 13, wherein the two or more other metals comprise PGM.

15. A process according to any of claims 12 to 14, wherein the retained Pd is recovered by elution with ammonia or a nitrogen-containing eluant.

CHROMATOGRAPHIC MEDIUM

Abstract

A chromatographic medium comprises thioether ligands bound to a solid cross-linked polymer matrix. The polymer is and organic polymer and the medium is hydrophilic. A method of manufacturing the media is also described. The media are useful in the chromatographic separation of components from solution, and in particular for the interseparation of platinum group metals.

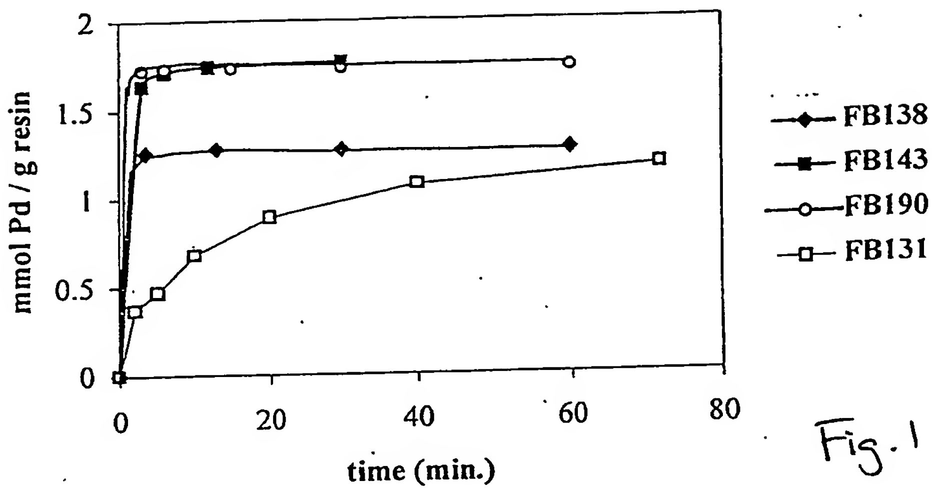

2
1.5
1
0.5
0
0
20
40
60
80
mmol Pd / g resin
time (min.)
FB138
FB143
FB190
FB131

Fig. 1

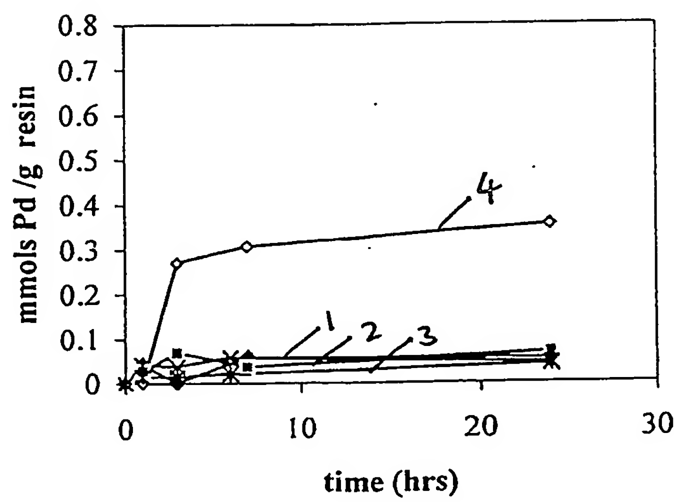

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
mmols Pd /g resin
time (hrs)
4
1
2
3

Fig. 2

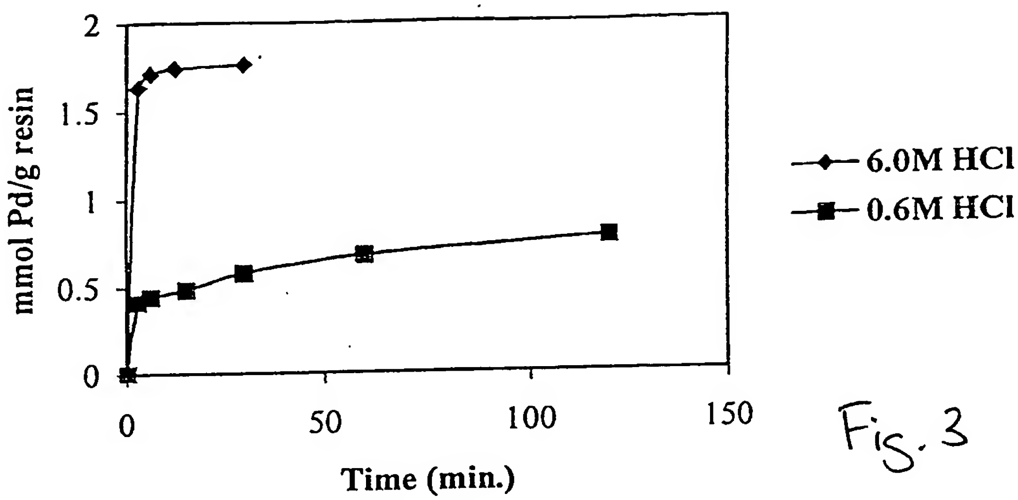

2
1.5
1
0.5
0
0
50
100
150
mmol Pd/g resin
Time (min.)
6.0M HCl
0.6M HCl

Fig. 3

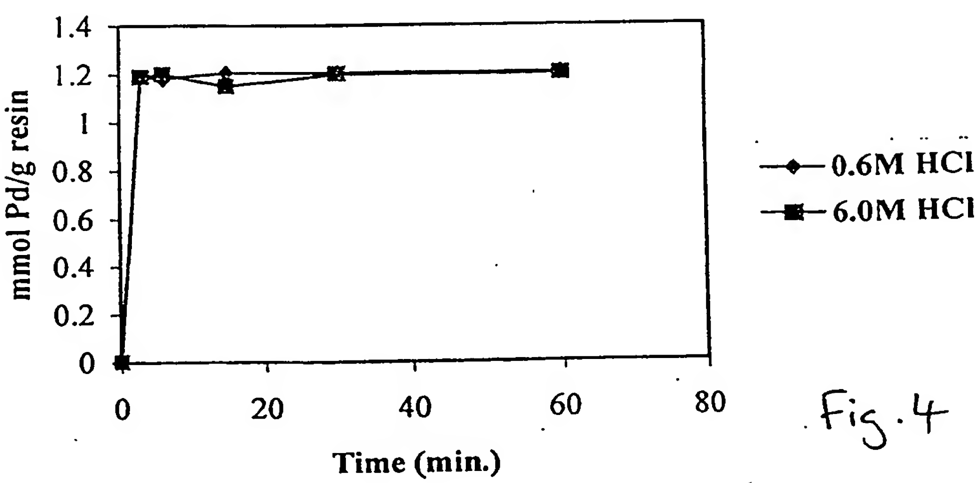

1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
20
40
60
80
mmol Pd/g resin
Time (min.)
0.6M HCl
6.0M HCl

Fig. 4

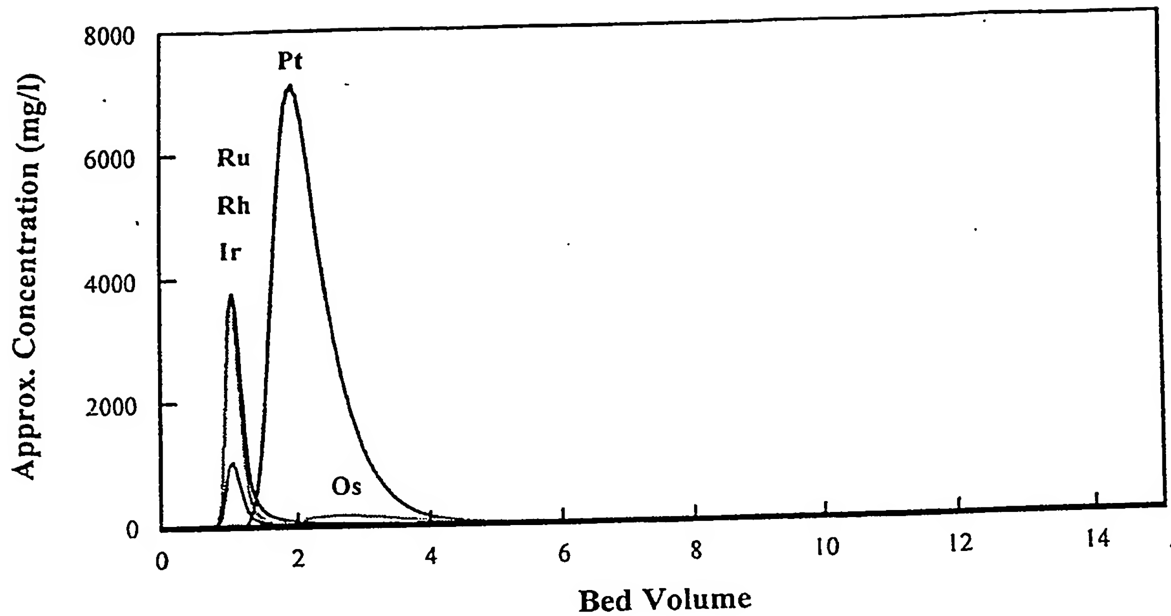

8000
6000
4000
2000
0
Approx. Concentration (mg/l)
Pt
Ru
Rh
Ir
Os
0
2
4
6
8
10
12
14
Bed Volume

Fig. 5

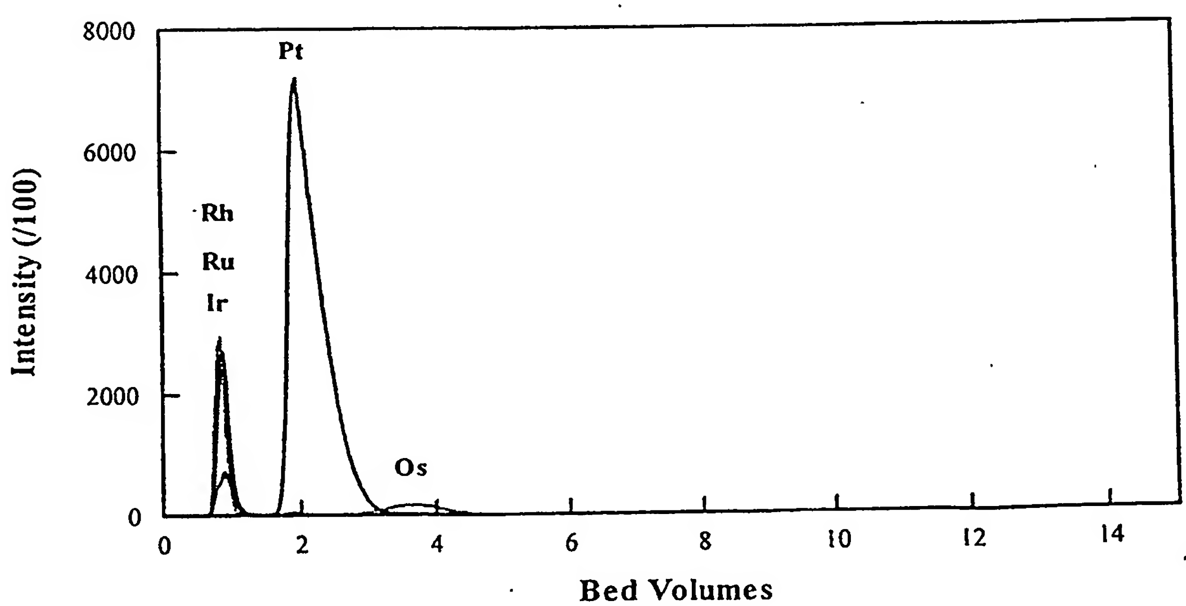

8000
6000
4000
2000
0
Intensity (/100)
Pt
Rh
Ru
Ir
Os
0
2
4
6
8
10
12
14
Bed Volumes

Fig. 6

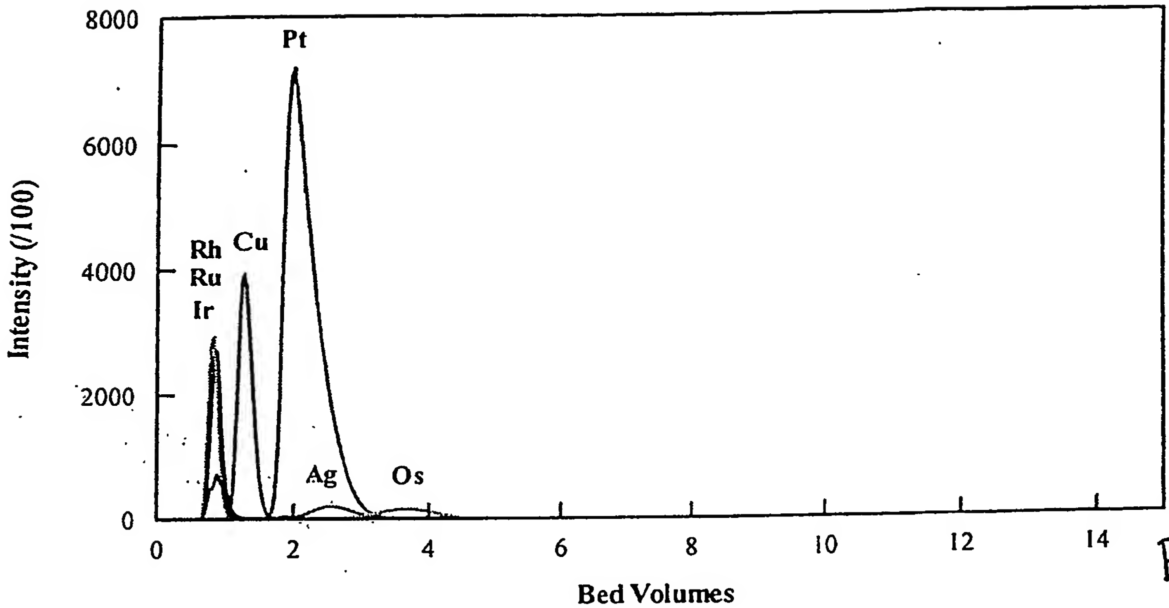

8000
6000
4000
2000
0
Intensity (/100)
Pt
Rh
Ru
Ir
Cu
Ag
Os
0
2
4
6
8
10
12
14
Bed Volumes

Fig. 7

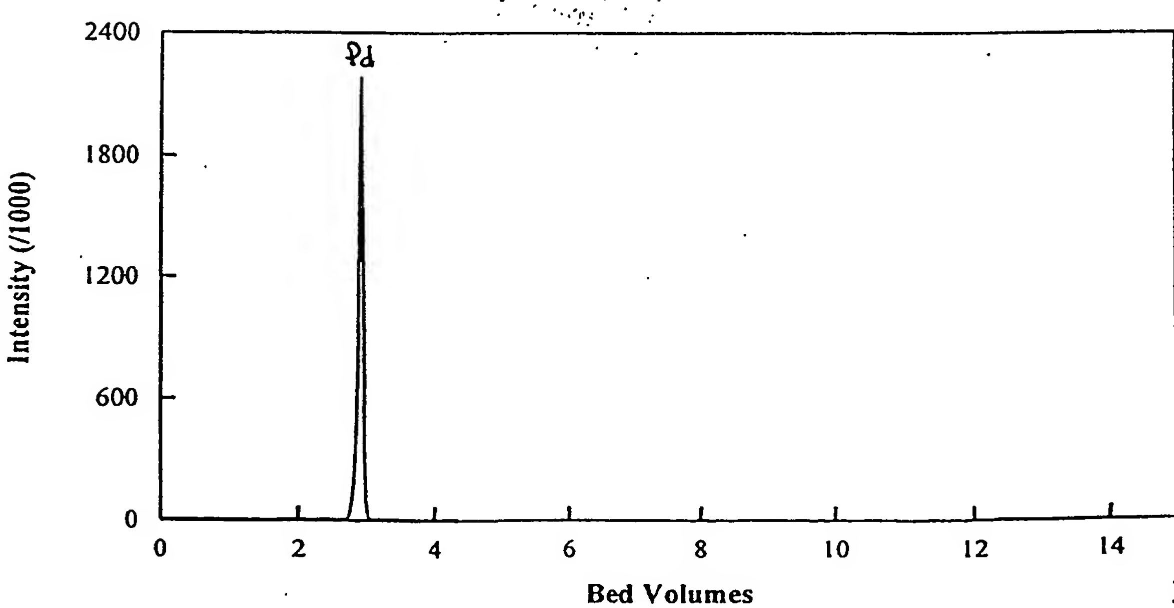

2400
1800
1200
600
0
Intensity (/1000)
Pd
0
2
4
6
8
10
12
14
Bed Volumes

Fig. 8